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Condensation Reaction of Ferrocene with Carbonyl Compounds

Mikio Shiga, Izumi Motoyama and Kazuo Hata

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo

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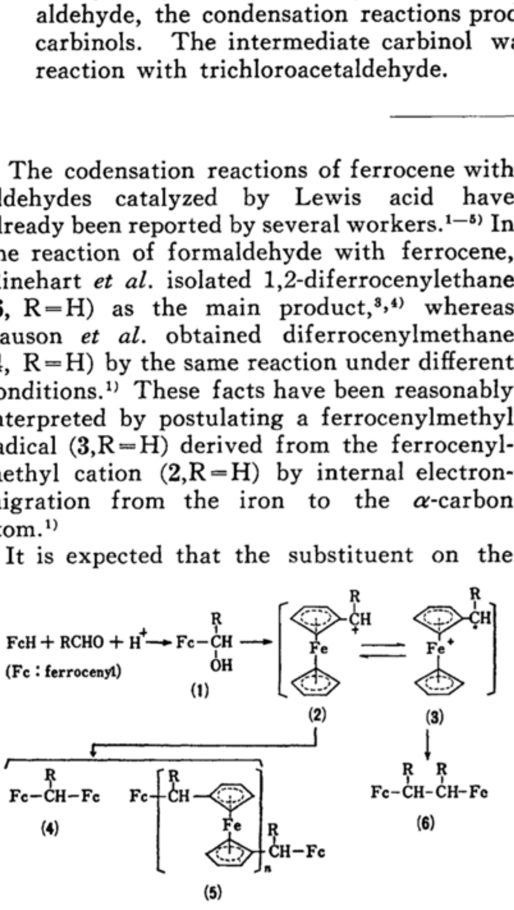
The condensation reactions of ferrocene with various ketones and with trichloroacetaldehyde in the presence of aluminum chloride were investigated. The formation of carbinol (**7**) as an intermediate was postulated in these reactions. In the reaction of acetone with ferrocene, the intermediate carbinol underwent further condensation with other ferrocene molecules to give oligomers (**9**). On the other hand, in the cases of methyl ethyl ketone, acetophenone, propiophenone, cyclohexanone, and trichloroacetaldehyde, the condensation reactions produced olefinic compounds *via* the intermediate carbinols. The intermediate carbinol was isolated together with the olefin in the reaction with trichloroacetaldehyde.

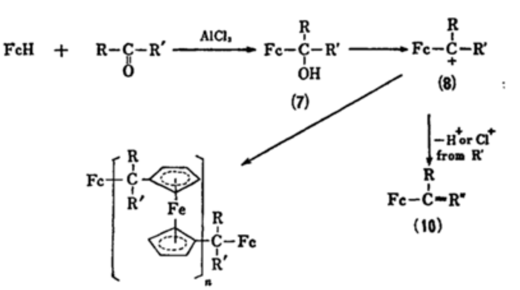
The codensation reactions of ferrocene with aldehydes catalyzed by Lewis acid have already been reported by several workers.[1—5] In the reaction of formaldehyde with ferrocene, Rinehart *et al.* isolated 1,2-diferrocenylethane (**6**, R=H) as the main product,[3,4] whereas Pauson *et al.* obtained diferrocenylmethane (**4**, R=H) by the same reaction under different conditions.[1] These facts have been reasonably interpreted by postulating a ferrocenylmethyl radical (**3**,R=H) derived from the ferrocenylmethyl cation (**2**,R=H) by internal electron-migration from the iron to the α-carbon atom.[1]

It is expected that the substituent on the α-carbon of the intermediate carbinol (or carbonium ion) will electronically affect such an electron-migration process. To date, however, few papers have been published on the reaction of ferrocene with ketone and polyhaloaldehyde. This paper will report on the condensation reactions of ferrocene with various ketones and with trichloroacetaldehyde in the presence of aluminum chloride.



Results and Discussion

The reaction of ferrocene with acetone in the presence of aluminum chloride in anhydrous chloroform under an atmosphere of nitrogen at room temperature gave a mixture of oligomers (**9**). The formation of such polycondensation products suggests that the reaction proceeded through a carbonium ion (**8**), derived from carbinol (**7**), as is shown in the scheme.



(**9**) R=R'=CH_3, n=1–7

(**9'**) R=R'=CH_3, n=1–6

(**9''**) R=R'=CH_3, n=7

	R	R''
a	CH_3	$CHCH_3$
b	C_6H_5	CH_2
c	C_6H_5	$CHCH_3$
d	1-cyclohexenyl	
e	H	CCl_2

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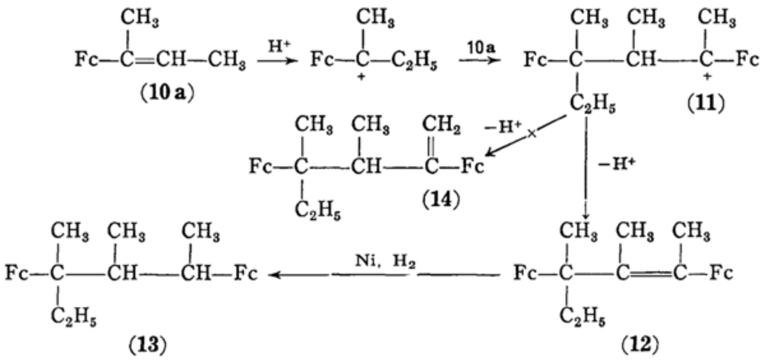
[1] P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, **1962**, 3880.

[2] E. W. Neuse and D. S. Trifan, *J. Am. Chem. Soc.*, **85**, 1952 (1963).

[3] K. L. Rinehart and C. J. Michejda, *ibid.*, **81**, 3162 (1959).

[4] K. L. Rinehart and C. J. Michejda, *Angew. Chem.*, **72**, 38 (1960).

[5] A. N. Nesmeyanov and I. I. Kritskaya, *Izvestia Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, **1962**, 352.



In the case of the reaction with methyl ethyl ketone, only 2,4-diferrocenyl-3,4-dimethyl-2-hexene (**12**) (mp 47—52°C) was isolated. The structure of **12** was supported by the IR spectrum. An absorption band at the 1625 cm^{-1} of **12** due to the ethylenic bond disappeared upon its catalytic hydrogenation to the alkane **13**, mp 41—49°C. It is most likely that the product **12** was produced as a result of the dimerization of an olefin **10a**, which was expected to arise upon the dehydration of the carbinol **7**, although it could not be isolated in this experiment. An alternative structure **14** for **12** was excluded by its IR spectrum.

Acetophenone also gave a dimerized product, 1,3-diferrocenyl-1,3-diphenyl-1-butene (**15**), mp 137.5—138.5°C. The NMR spectrum of **15** shows the integrated intensity ratio of the protons in ferrocenyl : phenyl and olefinic (overlapped) : methyl to be 18.3 : 11.2 : 3.0, which is nearly equal to that calculated on the basis of the formula **15**. An alkane **16**, mp 118—126°C, was obtained quantitatively by the hydrogenation of the dimer **15**. The formation of the dimer **15** may be interpreted through a mechanism analogous to that for the dimer **12**.

Neither of these reactions gave any oligomeric product, unlike the reaction of acetone with ferrocene. The absence of oligomeric products in these reactions strongly suggests that no electrophilic attack of the carbonium ion **8**, which might be created from the carbinol **7**, occurred on the other ferrocene nuclei during these reactions. Therefore, the carbinol or the carbonium ion might, upon the elimination of the water molecule or the α-proton, be converted into the two olefins, **10a** and **10b**, which would be immediately dimerized to **12** and **15** respectively by the action of aluminum chloride and a trace of water.

The condensation reaction of propiophenone with ferrocene gave only an olefinic product, 1-ferrocenyl-1-phenylpropene **10c**, a part of which was oxidized, when chromatographed on alumina, to give benzoylferrocene (**18**), mp 111—112°C. When it was refluxed with a Raney nickel catalyst in methanol,[6] the olefin **10c** was converted almost quantitatively into the hydrogenated product **17** (mp 59—60°C), which was identified by comparing it with the authentic sample prepared from the reaction of benzoylferrocene with ethylmagnesium bromide, followed by treatment with zinc dust and hydrochloric acid.[7] The NMR

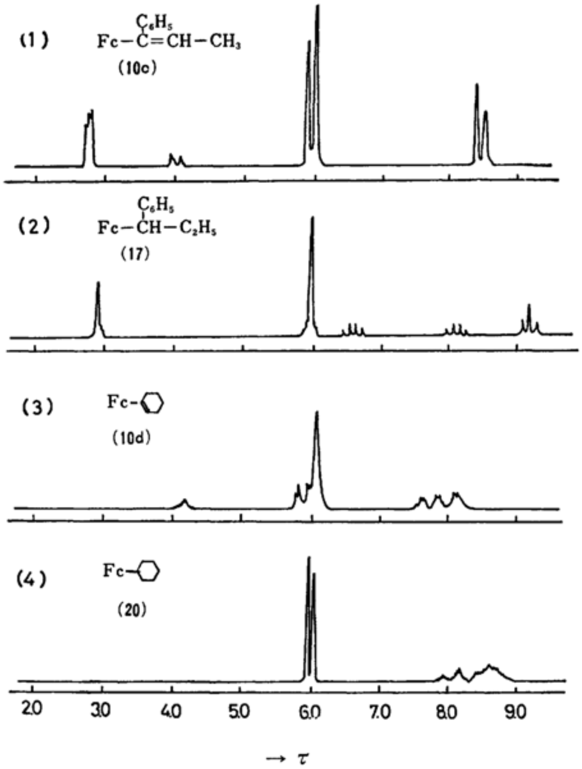


Fig. 1 The NMR spectra of the products.

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[6] K. Sakai, T. Ito and K. Watanabe, This Bulletin, **39**, 2230 (1966).

[7] G. L. K. Hoh, W. E. McEwen and J. Kleinberg, *J. Am. Chem. Soc.*, **83**, 3949 (1961).

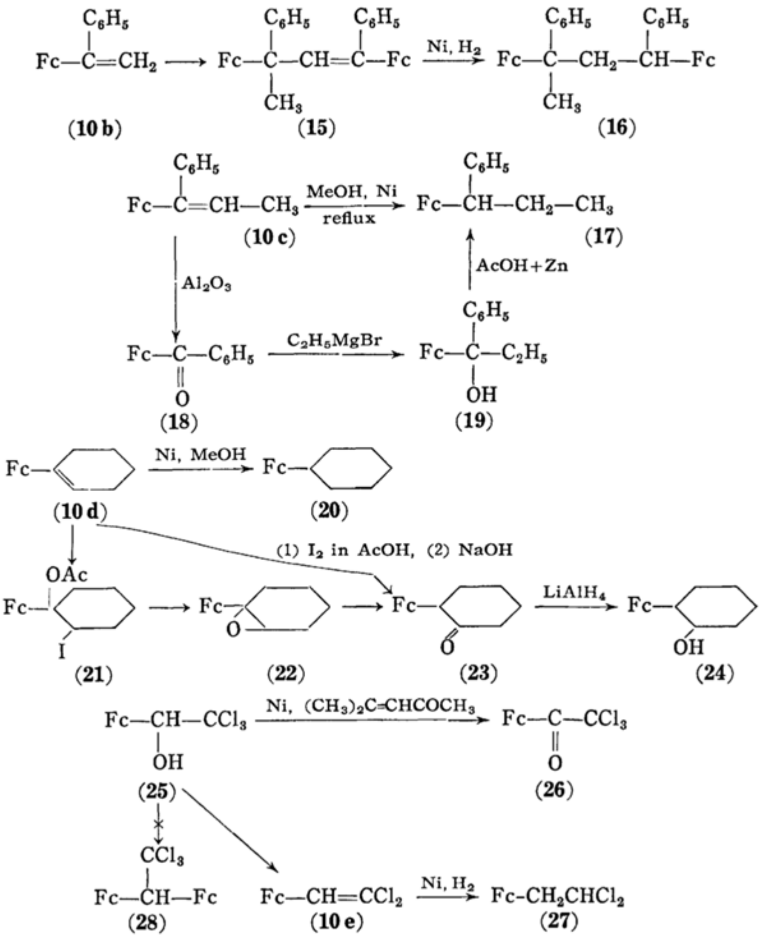
TABLE 1. THE NMR SPECTRA OF CONDENSATION PRODUCTS AND THEIR DERIVATIVES (τ-Value, in $CDCl_3$)

Compound	Cyclopentadienyl ring protons			CH_3	CH_2	CH	-C=CH-	C_6H_5	OH
	2,5-	3,4-	Unsubstd.						
15	5.74(s) (··········18.3··········)*	5.84(s)	5.92(d)	8.5(s) (3)*			3.4 (·········11.2·········)*	2.86(m)	
10c	·········5.93(s)········· (·······4.1·······)		6.02(s) (5.1)*	8.49(d) (3)*			6.02(m) (0.9)*	2.76(m) (5.2)*	
17	··········6.06·········· (··········8.6··········)*			9.2(t) (3)*	8.13 (1.7)*	6.59(q) (1.1)*		2.85(m) (4.9)*	
10d	5.80(t) (2)*	5.95(t) (2.1)*	6.03(t) (5.2)*		7.75(b) 8.02(b) 8.35(b) (8.2)$^{a)}$*		4.2(m)		
20	·········6.06(s)········· (·······4.0·······)		6.01(s) (5.2)*		8.17(b) 8.70(b) (·········10.7·········)*	8.17(b)			
10e	5.44(t) (2.1)*	5.72(t) (2)*	5.82(s) (5.1)*				3.43(s) (1.1)*		
25	·········5.53(t)········· (2)*	(·········6·8·········)*	5.80(s)			5.20(s) (1.1)*			7.13(s) (1.1)*

a) The observed methylene proton signals at $C_{4,5}$, C_3 and C_6 in compound **10d** were 3.9 : 2.2 : 2.1.

* The figures in parentheses shown below each τ-value indicate the corresponding integrated intensity ratios.

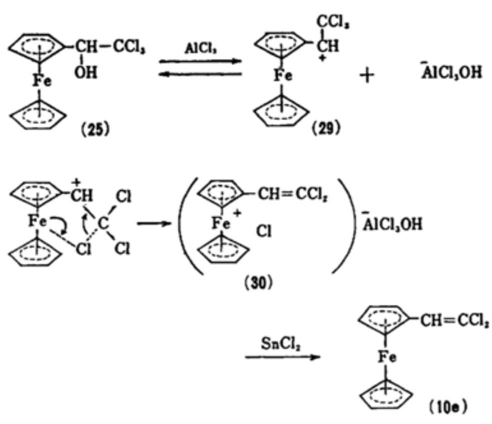
The figures shown between ······ indicate those for overlapped peaks.



spectrum of **10c** had a doublet peak at τ 8.49 for methyl protons and two singlets, at τ 5.93 and τ 6.02, for the substituted cyclopentadienyl ring protons and the unsubstituted ones respectively, as is shown in Table 1 and Fig. 1-(1). The NMR signal due to the methyl protons of **17** showed a higher τ-value (τ 9.2, triplet) than that of **10c**. An analogous tendency was observed also in the resonance peaks of ring protons between these two compounds.

The reaction of cyclohexanone with ferrocene afforded cyclohexenylferrocene (**10d**), mp 67—68°C, in a good yield (96%). The olefin **10d** was quantitatively converted to cyclohexylferrocene (**20**), mp 40—41°C, when it was refluxed with a Raney nickel catalyst in methanol. The NMR spectrum of **10d** showed three triplets assignable to the 2,5- and 3,4-protons of the substituted cyclopentadienyl ring and the five protons of the unsubstituted ring respectively, whereas in the hydrogenated product **20** these three triplets changed into two singlets, at τ 6.06 and τ 6.01, corresponding to those of the substituted and the unsubstituted rings respectively, as is shown in Figs. 1-(3) and 1-(4). Cyclohexenylferrocene (**10d**) was transformed into 2-ferrocenylcyclohexanone (**23**), mp 99—101°C, probably through the intermediates **21** and **22**, when treated with iodine in glacial acetic acid and then with aqueous alkali. The reduction of the product **23** with lithium aluminum hydride gave 2-ferrocenylcyclohexanol (**24**), mp 88—90°C.

Trichloroacetaldehyde condensed with ferrocene to give 1,1-dichloro-2-ferrocenylethylene (**10e**), mp 55.5—56.5°C, and trichloromethylferrocenylcarbinol (**25**). The IR spectrum of the latter showed that the OH stretching band shifted toward a lower-frequency region (3430 cm^{-1}), suggesting the presence of intramolecular hydrogen-bonding between the hydroxyl group and the iron atom. The integrated intensity ratios in the NMR spectra of the olefin **10e** and the carbinol **25** were found to be as shown in Table 1. They are nearly equal to the values calculated on the basis of the formulas **10e** and **25**. When the carbinol **25** was heated with mesityl oxide in the presence of a Raney nickel catalyst, a mild redox reaction[6] afforded the corresponding ketone **26**, which sublimes easily. The olefin **10e** was catalytically hydrogenated in methanol to 1,1-dichloro-2-ferrocenylethane (**27**). The fact that the expected product **28** could not be isolated in the reaction of trichloroacetaldehyde with ferrocene can not simply be explained in terms of the steric effect of substituents on the also-expected carbonium ion **29**. On the other hand, it has been suggested that the participation of the iron atom may facilitate the formation of the olefin from the carbonium ion **29** through the ferricinium ion **30**, as is shown in the scheme.[8]



The fact that the intermediate carbinol was isolated only in the case of trichloroacetaldehyde indicates that the formation of the carbonium ion was retarded by the strong electron-withdrawing nature of the trichloromethyl group in the carbinol **25**. The extraordinary stability of the ferrocenylmethyl carbonium ion (**2**, $R=CH_3$) over the phenyl analog has previously been demonstrated in many cases,[9,10] and it is considered that the carbonium ion can be an important intermediate in the condensation reaction of ferrocene with a carbonyl compound, although there is no positive evidence that the carbonium ion was produced during any reaction except in that with acetone.

The results described above indicate that the presence of a substituent on the α-carbon of the intermediate carbonium ion facilitates the formation of olefin and seems to prevent the formation of a radical from the carbonium ion by electron-migration.

Experimental

General Procedure. The reaction conditions and the products of the condensation reactions of ferrocene and carbonyl compounds are summarized in Table 2. A typical reaction procedure was as follows: To 0.16 mol (24 g) of anhydrous aluminum chloride in 20 m*l* of chloroform at 0°C, under an atmosphere of nitrogen, there was slowly added

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[8] M. Rosenblum, J. O. Santer and W. G. Howells, *J. Am. Chem. Soc.*, **85**, 1450 (1963).

[9] J. H. Richards and E. A. Hill, *ibid.*, **81**, 3484 (1959).

[10] D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, **1960**, 1.

TABLE 2. CONDENSATION REACTION OF FERROCENE WITH CARBONYL COMPOUNDS

Carbonyl compound	Time (hr)	Product	Mp (Bp) (°C)	Yield (g)	Yield (%)
Acetone	20	Oligomers (**9′**)	oil	6.5	—
		(**9″**)	162—168	2.2	—
Methyl ethyl ketone	3	2,4-Diferrocenyl-3,4-dimethyl-2-hexene (**12**)	47—52	7.9	62
Acetophenone	5	1,3-Diferrocenyl-1,3-diphenyl-1-butene (**15**)	137.5—138	4.3	32
Acetophenone	20	1,3-Diferrocenyl-1,3-diphenyl-1-butene (**15**)	137.5—138	8.5	55
Propiophenone	5	1-Ferrocenyl-1-phenylpropene (**10c**)	(105—110/ 0.4 mmHg)	7.1	44
Cyclohexanone	5	Cyclohexenylferrocene (**10d**)	67—68	13.7	96
Trichloroacetaldehyde	20	1,1-Dichloro-2-ferrocenylethylene (**10e**)	55.5—56.5	3.1	21
		Trichloromethylferrocenylcarbinol (**25**)	140—141	0.85	5

In each reaction, 10 g (0.054 mol) of ferrocene was treated with 0.16 mol of carbonyl compounds in the presence of 24 g (0.16 mol) of $AlCl_3$ at 0°C.

0.16 mol of the respective carbonyl compound. Subsequently, 0.054 mol (10 g) of ferrocene, dissolved in 30 m*l* of chloroform, was added dropwise to the mixture with good stirring. After it had been stirred for several hours at room temperature, the reaction mixture was poured into 200 m*l* of water containing 5 g of stannous chloride, and then stirred for another 30 min. Finally, the chloroform layer which separated from the aqueous layer was washed three times with 50-m*l* portions of water and dried over anhydrous magnesium sulfate. Then, the chloroform and the unreacted carbonyl compound were removed by distillation to give a crude reaction product. The subsequent treatment and purification were conducted in different ways for the different products, as will be described below.

Isolation of Oligomers 9′ and 9″. The red brown oil (11.5 g), obtained from the reaction of acetone (9.3 g) with ferrocene (10 g) was dissolved in 2 m*l* of chloroform, and then the solution was poured into 200 m*l* of methanol. After the mixture had been kept standing overnight, 2.5 g of a yellow solid separated as a precipitate. The recrystallization of the precipitate from $CHCl_3$-CH_3OH gave 2.2 g of a yellow solid, mp 162—168°C.

Found: C, 68.95; H, 5.98%; mol wt(Rast), 2010. Calcd for the formula **9″**: C, 68.60; H, 6.11%; mol wt, 1944.

By the evaporation of the solvent from the filtrate, 6.5 g of an amber liquid was obtained.

Neither of these compounds showed any olefinic absorption band in its IR spectrum. The amber liquid was assumed to be a mixture of oligomers (**9′**) with lower molecular weights.

2,4-Diferrocenyl-3,4-dimethyl-2-hexene (12). The condensation product of the reaction of methyl ethyl ketone (11.6 g) with ferrocene (10 g) was extracted with methanol in a Soxhlet extractor for three hours. Then, the residual, insoluble part in methanol was dissolved in 2 m*l* of chloroform and the solution was poured into 200 m*l* of methanol. A yellow solid (8.1 g) was thus obtained as a precipitate. It was recrystallized from $CHCl_3$-CH_3OH. Yield 7.9 g (62%), mp 47—52°C.

Found: C, 70.21; H, 5.48%; mol wt, 496. Calcd for $C_{28}H_{32}Fe$: C, 70.05; H, 6.67%; mol wt, 481.

2,4-Diferrocenyl-3,4-dimethylhexane (13). A solution of 2 g of 2,4-diferrocenyl-3,4-dimethyl-2-hexene (**12**) in 30 m*l* of methanol was refluxed for 3 hr in the presence of Raney Ni (1 g).⁶⁾ The reaction mixture was then allowed to cool to room temperature and filtered in order to remove the catalyst. The methanol solution was poured into 200 m*l* of water and extracted with chloroform. The extract was concentrated to a small volume and poured into 100 m*l* of methanol. Another treatment of the mixture in the way described above gave a solid. It was recrystallized from $CHCl_3$-CH_3OH to yield 1.98 g (98% yield) of a yellow product, mp 41—48°C. Its IR spectrum had no absorption band at 1625 cm^{-1}, a band which had been assigned in **12** to the ethylenic bond.

Found : C, 69.85; H, 7.10%; mol wt, 499. Calcd for $C_{28}H_{34}Fe$: C, 69.56; H, 7.03%; mol wt, 483.

1,3-Diferrocenyl-1,3-diphenyl-1-butene (15). The condensation of acetophenone with ferrocene gave **15**. The procedure was similar to that employed for the isolation of **12**. The crude product was recrystallized from ether after the removal of the unreacted ferrocene by sublimation to give 8.5 g (55% yield) of orange yellow crystals, mp 137.5—138°C.

Found: C, 74.87; H, 5.50%; mol wt, 570. Calcd for $C_{26}H_{32}Fe$: C, 74.79; H, 5.55%; mol wt, 577.

The reduction⁶⁾ of **15** was carried out in the way which has been described for **12**. Yellow crystals of 1,3-diferrocenyl-1,3-diphenylbutane (**16**), mp 118—126°C; (1.9 g, 98% yield) were obtained from 2 g of **15**.

Found: C, 74.12; H, 5.84%; mol wt, 582. Calcd for $C_{26}H_{34}Fe$: C, 74.53; H, 5.86%; mol wt, 579.

1-Ferroceny-1-phenylpropene (10c). The crude product (11.6 g), obtained from the condensation reaction of ferrocene (10 g) with propiophenone (21.6 g) was distilled under reduced pressure to give 7.1 g (44% yield) of **10c** as a reddish-brown liquid (bp 105—110°C/0.4 mmHg) ; this liquid partially decomposed when chromatographed on alumina to give benzoylferrocene (**18**), mp 111.5—112°C. This anomalous behavior of **10c** toward alumina was confirmed by repeated experiments, and the benzoylferrocene obtained in this reaction was identified by comparing it with an authentic sample.

Found: C, 75.41; H, 6.02%; mol wt, 305. Calcd for $C_{19}H_{18}Fe$ (**10c**): C, 75.49; H, 5.96%; mol wt, 302.

1-Ferrocenyl-1-phenylpropane (17). The olefinic compound **10c** was hydrogenated by the procedure described above, and the crude product was chromatographed on alumina to give 1.92g (98%) of yellow needles, mp 59—60°C.

Found: C, 74.92; H, 6.67%; mol wt, 309. Calcd for $C_{19}H_{20}Fe$: C, 75.04; H, 6.58%; mol wt, 304.

1-Ferrocenyl-1-phenylpropane (**17**) was also prepared[7] from benzoylferrocene (**18**) by the Grignard reaction with ethylmagnesium bromide and by the successive reduction of the product with zinc dust and hydrochloric acid.

Cyclohexenylferrocene (10d). The crude condensation product obtained from cyclohexanone (15.6 g) and ferrocene (10g) was chromatographed on alumina to give 13.7g (96%) of golden yellow crystals, mp 67—68°C. The IR spectrum of **10d** showed an olefinic absorption band at 1630 cm^{-1}.

Found: C, 72.06; H, 6.89%; mol wt, 264. Calcd for $C_{16}H_{18}Fe$: C, 72.23; H, 6.77%; mol wt, 266.

Cyclohexenylferrocene (**10d**) was treated with Raney Ni in the way described above, and the crude product was purified by chromatography on alumina to yield 1.19g (79%) of cyclohexylferrocene (**20**) as yellow crystals (mp 40—41°C).

Found: C, 71.69; H, 7.34%; mol wt, 265. Calcd for $C_{16}H_{20}Fe$: C, 71.69; H, 7.46%; mol wt, 268.

2-Ferrocenylcyclohexanone (23). A solution of 2g of cyclohexenylferrocene and 0.4g of iodine in 40 m*l* of glacial acetic acid was heated to 95°C for 1.5hr. After it had been cooled, the reaction mixture was added, drop by drop, to 200 m*l* of a 30% aqueous potassium hydroxide solution. The solution was stirred for 1 hr and then extracted with benzene. The extract was washed once with water and dried over anhydrous magnesium sulfate. After the drying agent had been removed, the solvent was distilled off. The residue was chromatographed on alumina, using benzene as a solvent, to yield 0.44g (21%) of orange yellow crystals, mp 99—101°C. The IR spectrum of this compound showed a sharp carbonyl band at 1685 cm^{-1}.

Found: C, 67.89; H, 6.19%; mol wt, 299. Calcd for $C_{16}H_{18}FeO$: C, 68.13; H, 6.38%; mol wt, 282.

2-Ferrocenylcyclohexanol (24). 2-Ferrocenylcyclohexanone (**23**) (0.5g), dissolved in 20 m*l* of anhydrous ether, was treated with lithium aluminum hydride in the usual way to afford a yellow solid (0.42g). Recrystallization from *n*-hexane gave 0.24g (48%) of yellow crystals, mp 88—90°C. Its IR spectrum showed a hydroxyl band at 3380 cm^{-1}.

Found: C, 68.33; H, 6.70%; mol wt, 262. Calcd for $C_{16}H_{20}FeO$: C, 67.60; H, 6.33%; mol wt, 284.

1,1-Dichloro-2-ferrocenylethylene (10e) and Trichloromethylferrocenylcarbinol (25). The dark orange solid product, obtained by the condensation of trichloroacetaldehyde (23.5g) with ferrocene (10 g), was chromatographed on alumina with chloroform. The first fraction afforded a mixture of 1,1-dichloro-2-ferrocenylethylene (**10e**) and unreacted ferrocene. After the removal of the ferrocene by sublimation, 4.2g of dark orange crystals were obtained. These crystals were purified by chromatography on alumina using benzene-*n*-hexane to give 3.1g(21%) of dark orange crystals, mp 55.5—56.5°C.

Found: C, 51.77; H, 3.72%; mol wt, 284. Calcd for $C_{12}H_{10}FeCl_2$: C, 51.46; H, 3.57%; mol wt, 280.

The second fraction of the chromatography yielded 0.91g of yellow crystals. Recrystallization from *n*-hexane gave 0.85g (5%) of yellow crystals, decomp. at 140—141°C, whose IR spectrum had a hydroxyl band at 3420 cm^{-1}.

Found: C, 43.48; H, 3.21%; mol wt, 329. Calcd for $C_{12}H_{11}FeOCl_3$: C, 43.24; H, 3.33%; mol wt, 332.

Trichloromethyl Ferrocenyl Ketone (26). A solution of 1g of trichloromethylferrocenylcarbinol (**25**) and 0.5g of a Raney nickel catalyst in 15 m*l* of mesityl oxide was heated at 95°C for 5 hr.[6] After cooling, the catalyst was filtered off and the filtrate was distilled under reduced pressure to remove the mesityl oxide. Subsequently, the residue was chromatographed on alumina with benzene to obtain 0.41 g of red crystals from the first fraction. Purification by sublimation then gave 0.38g (38%) of red crystals, mp 84—86°C.

Found: C, 44.21; H, 2.93%; mol wt, 335. Calcd for $C_{12}H_9FeOCl_3$: C, 43.66; H, 2.72%: mol wt, 330.

1,1-Dichloro-2-ferrocenylethane (27). 1,1-Dichloro-2-ferrocenylethylene (**10e**) was treated by the same procedure as has been described for the reduction of **12**. The crude product was purified by chromatography on alumina with *n*-hexane to give 1.84g (92%) of an amber liquid product **27**.

Found: C, 52.11; H, 4.87%; mol wt, 278. Calcd for $C_{12}H_{12}FeCl_2$: C, 51.06; H, 4.25%; mol wt, 282.

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